Study of the acetonitrile poisoning of platinum cathodes on proton exchange membrane fuel cell spatial performance using a segmented cell system

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Abstract

Due to the wide applications of acetonitrile as a solvent in the chemical industry, acetonitrile can be present in the air and should be considered a possible pollutant. In this work, the spatial proton exchange membrane fuel cell performance exposed to air with 20 ppm CH₃CN was studied using a segmented cell system. The injection of CH₃CN led to performance losses of 380 mV at 0.2 A cm⁻² and 290 mV at 1.0 A cm⁻² accompanied by a significant change in the current density distribution. The observed local currents behavior is likely attributed to acetonitrile chemisorption and the subsequent two consecutive reduction/oxidation reactions. The hydrolysis of CH₃CN and its intermediate imine species resulted in NH₄⁺ formation, which increased the high-frequency resistance of the cell and affected oxygen reduction and performance. Other products of hydrolysis can be oxidized to CO₂ under the operating conditions. The reintroduction of pure air completely recovered cell performance within 4 h at 1.0 A cm⁻², while at 0.2 A cm⁻² the cell recovery was only partial. A detailed analysis of the current density distribution, its correlation with spatial electrochemical impedance spectroscopy data, possible CH₃CN oxidation/reduction mechanisms and mitigation strategies are presented and discussed.

Key words: PEMFC; Pt cathode; Acetonitrile; Airborne contaminant; Segmented cell; Spatial EIS

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1. Introduction

Forthcoming mass production of proton exchange membrane fuel cells (PEMFCs) as electrochemical replacements of internal combustion engines and portable power generation brings up questions regarding the durability, reliability and high performance of fuel cells under different environmental conditions. Air is the most practical and economic oxidant for fuel cell operations; however, air may contain inorganic and organic impurities. Industrial and automotive vehicle exhausts contain the major contaminants (SO_2 , NO_x , NH_3 and H_2S). Additionally, a few natural processes, such as volcanic activity, negatively affect air quality. These inorganic air pollutants are known to cause significant PEMFC performance losses and even degradation.

The effects of major inorganic airborne contaminants have been intensively studied [1-11]. Sulfur dioxide and hydrogen sulfide have been shown to cause drastic decreases in PEMFC performance, which can only be partially recovered by reintroducing pure air into the cathode gas stream [1, 2, 5-15]. Sulfur-containing impurities easily adsorb onto the Pt cathode, significantly decreasing the Pt electrochemical area (ECA) and oxygen reduction activity and increasing H_2O_2 formation, which accelerates electrolyte degradation [7, 12, 13]. The effects of nitrogen-containing air contaminants (e.g., NO_x and NH_3) were found to be moderate and recoverable [1, 2, 6, 7, 9, 10, 16-23]. PEMFC exposure to NaCl solutions resulted in performance degradations due to the negative impact of Cl^- on the Pt ECA [24, 25].

A few organic compounds were studied as possible airborne pollutants for PEMFCs. The chemical warfare agents (sarin, sulfur mustard, cyanogen chloride and hydrogen cyanide) seriously compromised PEMFC performances in irreversible manners [1]. Benzene, toluene and 1,3-butadiene also caused performance decreases, but the losses were recovered [2, 26]. To expand the list of

studied airborne organic pollutants, seven compounds were chosen from 260 possible air contaminants suggested by the Environmental Protection Agency [27]. The list includes acetylene, propene, methyl methacrylate, 2-propanol, bromomethane, naphthalene and acetonitrile. These compounds are widely used as solvents (CH_3CN , $\text{i-C}_3\text{H}_8\text{OH}$), synthesis precursors in the chemical industry (C_2H_2 , $\text{CH}_3\text{C}(\text{CH}_3)\text{COOCH}_3$, C_3H_6 , CH_3CN), welding fuels (C_2H_2), and fumigants (CH_3Br , C_{10}H_8). All seven contaminants have been found to cause serious PEMFC performance losses and have significant impacts on ORR [28, 29].

Acetonitrile is a volatile, highly polar solvent used to extract fatty acids, animal/vegetable oils and butadiene. It is also a well-known solvent for spinning synthetic fibers and in casting and molding plastics. It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes. In laboratories acetonitrile is applied in high-performance liquid chromatography, as a solvent for electrochemistry, DNA synthesis and peptide sequencing. Based on the broad industrial applications for acetonitrile, it can be prevalent at industrial sites and should be considered as a possible air pollutant because it will affect the PEMFC.

The electrochemisorption and reactivity of acetonitrile at platinum electrodes have been of primary interest in the fundamental study of electrocatalysis [30-35]. The effects of acetonitrile on the co-adsorption of hydrogen and oxygen are important for understanding electrochemical hydrogenation and oxidation reactions. The study of the electrochemical behavior of nitriles (CH_3CN and $\text{C}_6\text{H}_5\text{CN}$) provides valuable information because of 1) the use of nitriles as electrochemically “inactive” aprotic solvents, 2) the involvement of nitriles in organic oxidation processes where nitrilium ions and amides can be formed, and 3) in reductive dimerization [31, 36-43]. Moreover,

the ORR in acetonitrile solutions have been intensively studied using rotating disk electrode (RDE), rotating ring disk electrode (RRDE) and cyclic voltammetry (CV) techniques [44-47].

The evaluation of fuel cell performance with a single cell does not reveal the spatial behavior of a PEMFC. In contrast, a segmented cell system provides locally resolved voltage, current and impedance data. It is a powerful tool for understanding the details of fuel cell operations under different conditions [48-55], the detection of membrane electrode assembly (MEA) defects [56, 57], hydrogen recirculation [58], and hydrogen stream CO poisoning [59-65]. Information about the current distribution when exposed to organic airborne pollutants is crucial to understanding the poisoning mechanism, improving the PEMFC environmental adaptability and developing useful mitigation strategies. This paper focuses on the detailed spatial performance studies of a fuel cell exposed to 20 ppm CH_3CN and operated at different current densities. Additionally, spatial electrochemical impedance spectroscopy (EIS) was employed to understand and characterize the local PEMFC response under exposure to acetonitrile.

2. Experimental

The experiments were conducted at a Grandalytics single fuel cell test station using a segmented cell system [54]. This diagnostic tool continues the previous works [49, 50, 66, 67] and allows simultaneous rather than sequential measurements of spatial EIS, spatial linear sweep voltammetry (LSV) and CV to be performed. The system has ten current channels in a high (standard) current mode and ten channels in a low current mode. The standard current mode enables the measurement of segment currents up to 15 A. The low current mode yields current measurement up to 375 mA, which is typical for CV and LSV experiments.

The segmented cell hardware was based on 100 cm² cell design. The hardware contained a segmented flow field, which consisted of ten cell segments forming a continuous path along ten parallel serpentine channels. Each segment had an area of 7.6 cm² and had its own distinct current collector and gas diffusion layers (GDL). The same channel designs were used for the segmented cathode and standard anode flow fields (the reactant streams were arranged in a co-flow configuration). The segmented cell hardware was applicable to either the anode or the cathode.

The segmented cell was operated with a commercially available 100 cm² MEA provided by Gore. The anode and cathode were made of Pt/C catalysts with a loading of 0.4 mg_{Pt} cm⁻². Sigracet 25 BC was used as the anode and cathode GDLs. The cathode used a segmented GDL and gasket configuration, whereas a single GDL was applied at the anode, and the total active area of the MEA was 76 cm². The gasket material was made of Teflon, with thicknesses of 125 μm for the anode and the cathode.

During CH₃CN exposure, the dry contaminant gas was injected into a humidified air stream, which was maintained at a constant level by increasing the temperature setting of the humidifier unit. The anode/cathode testing conditions for the contamination experiments were H₂/air, at a 2/2 stoichiometry, a 100/50% relative humidity and a 48.3/48.3 kPa_g backpressure. The cell temperature was 80°C. The MEA was operated under galvanostatic control of the whole cell current in the range of 0.1-1.6 A cm⁻² (based on the 76 cm² of the active MEA area).

The polarization curves (VI curves) in the H₂/air gas configuration were measured under the same conditions as the contamination experiment. VI curve measurements were also performed in the

H₂/He+O₂ (21 vol.%) and H₂/O₂ gas configurations and under galvanostatic control of the total cell current. To maintain a constant water transport in the cell for any given total cell current density, the flow rates of H₂/He+O₂ and H₂/O₂ were identical to those used during the H₂/air operation with a stoichiometry of 2. Consequently, the stoichiometry of He+O₂ remained at 2, whereas the stoichiometry of O₂ increased to 9.5. The resulting three different VI curves (H₂/air, H₂/He+O₂ and H₂/O₂) were used for the determination of the activation, ohmic and mass transfer (permeability and diffusion) overpotentials of a segment, as previously described [54].

The VI curve measurements and contamination experiments were combined with EIS to determine the high-frequency resistances (HFR) of the cell and segments and to record the impedance spectra for all ten segments and the overall cell. The selected frequency range for the EIS experiments was 0.05 Hz to 10 000 Hz, and the amplitude of the sinusoidal current signal perturbation was 2 A, which resulted in a cell voltage response of 10 mV or lower. The HFR was determined from the intercept of the EIS with the x-axis at higher frequencies of the Nyquist plot.

CV experiments were conducted for the determination of the ECA using a Solartron SI 1287/electrochemical interface. The CV experiments were performed at a cell temperature of 35°C with a scan rate of 20 mV s⁻¹, while 100% humidified hydrogen and nitrogen were supplied to the reference/counter and working electrodes, respectively, at a flow rate of 0.750 l min⁻¹. For each measurement, three cycles were applied over a potential range from -0.015 to 1.1 V vs. the hydrogen reference electrode (HRE). The hydrogen desorption peak area of the third cycle was used to determine the ECA. Hydrogen crossover experiments were performed at the same temperature and flow conditions as the ECA experiments using an LSV from 0.1 to 0.4 V vs. the HRE at a scan rate of 0.1 mV s⁻¹.

The segmented cell was assembled using established procedures, conditioned and subjected to a set of diagnostic tests. The beginning of test (BOT) diagnostics consisted of a CV to determine the ECAs of the electrodes, an LSV to determine the hydrogen crossover current of the cell and a measurement of the VI curves with spatial EIS using the H₂/air, H₂/He+O₂ and H₂/O₂ gas configurations to determine the performance and overpotential distributions of the cell and impedance responses [54, 56, 57]. The same diagnostic tests (end of test (EOT)) were repeated after the CH₃CN experiment.

3. Results

3.1. Fuel cell operation at high current density

Fig. 1 presents profiles of the segment voltages, current densities normalized to their initial values and HFR vs. experiment time at 1.0 A cm⁻². For the first 15 h, the cell was operated with pure air resulting in a cell voltage of 0.660-0.670 V. The initial current density distribution was in the 1.15 to 0.85 A cm⁻² range for segments 1 and 10. The injection of 20 ppm of CH₃CN significantly decreased the voltage during the transition period, which lasted 3-4 h. The voltage eventually reached 0.380 V at steady state as previously reported [28]. The voltage loss was 0.285-290 V, and noticeable changes were observed in the current density distribution.

The local currents went through several redistribution processes. At a first stage, the current densities of inlet segments 1-5 immediately decreased, while the current densities of outlet segments 6-10 increased. A second stage started 9-10 minutes after the contamination: segments 1-5 demonstrated increases in the current density, and segments 6-10 showed decreases in performance. Thus, a reversal of the local current order was observed, which may have been indicated in the

changes to the CH₃CN transformation mechanisms on the Pt electrodes via changes in the cell voltage, current and level of water production. The current density distribution progressed through a transition point corresponding to the slope minima of the voltage and current density profiles after 1.5-2 h of CH₃CN exposure. This point corresponded to a cell voltage of 0.480-0.500 V. The segments reached steady state after 5 h of acetonitrile exposure. At steady state, the inlet segments had greater performances than that of the outlet. The current density redistribution varied from +13% for segment 1 to -15% for segment 10 due to the operation of the cell in the galvanostatic mode, which required an overall constant current. This observation was different from previously observed spatial PEMFC performances when exposed to CO in a H₂ stream or C₂H₂ in air, where the performances of the inlet segments were lower than those of the outlet segments [59-65, 68]. It is likely that at steady state, CH₃CN impacted the inlet part of the MEA. However, products or intermediates of acetonitrile chemical/electrochemical conversion moved downstream with the produced water, accumulated and affected the ionomer, Pt surface and ORR at the outlet of MEA, resulting in a non-homogeneous performance.

The cell and segments almost recovered their performance within 5 h after stopping CH₃CN injection into the air stream within 5 h. These recoveries most likely occurred through similar processes, which were detected in the first hours of the exposure. The current density curves showed extremal points after 1.5 h of recovery, which corresponded to an inflection point in the voltage profiles at 0.520-0.550 V. Additionally, CH₃CN injection led to an increase in the HFR of the individual segments from 0.051-0.074 to 0.060-0.084 $\Omega \text{ cm}^2$.

The spatial EIS data for all ten segments and the overall cell recorded 1.0 A cm⁻² are presented in Fig. 2. The initial EIS spectra were recorded during the prepoisoning stage after operation with pure

air for 14 h. The EIS curves of the fuel cell that operated without any air impurities consisted of several arcs: a high-frequency arc, which can be distinguished at a low current operation; a high-frequency cathode loop due to a charge transfer resistance and a double layer capacitance of the ORR; and a low-frequency arc presenting mass transfer limitations at the cathode [69]. There was an increase in the diameter of the low-frequency mass transfer loop from the inlet to the outlet segments due to O₂ depletion and water accumulation [51, 52, 65].

After 1 h of CH₃CN injection, there was an increase in the cathode charge transfer and mass transfer resistances for segments 1-9 and a slight low-frequency inductance for all segments (Fig. 2). During the continuous injection of CH₃CN for 5 h, the impedance continuously increased, and steady state was reached at 10 h. Segment 10 did not show significant changes in the impedance response during the contaminant injection. In addition the exposure to acetonitrile resulted in an increase in the HFR for all segments. After 1 h of operation with pure air during the recovery stage, the HFR decreased, a slight impedance decrease was observed, and low-frequency inductive loops formed in all segments. These observations corresponded with the inflection points in the voltage (approximately 0.520 V) and current density profiles. The low-frequency inductive behavior in PEMFCs was previously observed during operations with H₂-containing CO [65, 70-72] and direct methanol fuel cells [73-75]. R.D. Armstrong and M. Henderson described a general mechanism consisting of two successive electron transfer steps involving the formation of an adsorbed intermediate species, which explained the appearance of low-frequency inductance under certain conditions [76]. Additional studies were performed by D.A. Harrington and B.E. Conway [77], Chu-Nan Cao [78], J.-P. Diard et al. [79] and P. Córdoba-Torres et al. [80]. The observation of low-frequency inductance during recovery at approximately 0.520 V allows us to assume that there were sequential reactions involving CH₃CN and its adsorbed species and the formation of an intermediate on the Pt

electrode. The continued operation with **pure** air led to a decrease in the impedance response, the disappearance of low-frequency inductance and the confirmed full recovery of the individual segments.

A comparison of the distributions of local voltage before (BOT) and after the contamination test (EOT) showed that acetonitrile exposure at 1.0 A cm^{-2} resulted in a spatial performance loss of 10-15 mV obtained for low current density operations ($0.1\text{-}0.2 \text{ A cm}^{-2}$) for segments 3-8. Performance losses of 15 mV were observed for segments 4 and 5 at high currents ($1.0\text{-}1.6 \text{ A cm}^{-2}$). An analysis of the overpotential losses [54] revealed that this performance loss was due to a slight increase in the activation overpotential caused by ECA decrease (7 and 15% for the anode and the cathode, respectively). Thus, the operation of a fuel cell at high current under CH_3CN exposure did not lead to serious cell damages. This may mitigate the negative impact of the contaminant and prevent degradation.

3.2. Fuel cell operation at low current density

Profiles of the voltages, normalized current densities and HFR of the segments recorded at total cell current densities of 0.2 A cm^{-2} are shown in Fig. 3. During the prepoisoning phase, the cell and segments voltages were 0.800-0.780 V, and the range of measured individual segment current densities was $0.18\text{-}0.24 \text{ A cm}^{-2}$.

The observed spatial performance was similar to the results obtained at 1.0 A cm^{-2} . It is possible to distinguish two cell poisoning stages. One hour after the injection of CH_3CN , the voltage dropped from 0.780 to 0.719 V, and the current had a lower performance in inlet segments 1-5 than those of the outlet segments of the MEA. The observed spatial current behavior was accompanied by an

increase in the HFR for segments 1-4 from 0.06 to 0.18 $\Omega \text{ cm}^2$. The local current distribution was -60% for segment 1 and +92% for segment 10. Further CH_3CN exposure caused a gradual decrease in the cell voltage, which reached a constant value of 0.420-0.430 V. At the same time, the current order of the segments changed at a cell voltage of approximately 0.480-0.500 V. Segments 1, 2 and 10 were characterized by higher performances, while the produced current declined in the other segments. The current densities in segments 5 and 8 nearly reached zero after cathode contamination within 90 h. The localized performance did not achieve steady state even after 105 h of acetonitrile exposure. The HFR of the individual segments also had similar trends as the current density profiles. The HFR decreased for segments 1, 2 and 10 to a value of approximately 0.08 $\Omega \text{ cm}^2$ and increased for the other segments. Segments 4, 5 and 8 had the highest HFR values of 0.179, 0.243 and 0.211 $\Omega \text{ cm}^2$, respectively, which were 3-5 times higher than their initial values.

The cell and segments only partially recovered, which required 5-6 h of operation with pure air. There was a performance loss of 90 mV after the CH_3CN poisoning test, and the local currents did not recover to their initial values. However, the recoveries at the low current densities seemed to be similar to the recoveries at the high current densities (Figs. 1 and 3). Extremum points were observed in the current profiles after 3-4 h of recovery, which corresponded to inflection points in the voltage profiles at 0.550 V. Moreover, operations with **pure** air decreased the HFR of the segments; only segments 1, 2 and 10 were restored to their original HFR values.

The spatial EIS data for all ten segments and the total cell during the poisoning and recovery stages are presented in Fig. 4. A comparison of the initial EIS data and the data under CH_3CN exposure revealed increases in the HFR and the charge and mass-transfer resistances for segments 1-7 after 1-10 h. The other segments did not demonstrate any significant changes (Fig. 4 a). Further poisoning

of the cell within 24-30 h resulted in an increase in the impedance response of all segments except segment 1, which showed a decrease in the charge and mass-transfer resistances. Decreases in the impedance values of segments 2-4 were observed after 55 h of exposure. However, only segments 1 and 2 presented further decreases in the HFR and charge and mass-transfer resistances. The other segments exhibited constant growth of impedance (Fig. 4 a), which agreed with the performance data shown in Fig. 3. The exposure to CH₃CN for 79-105 h resulted in significant increases in the impedances of segments 5 and 8, which accounted for their low performances.

A recovery with pure air for 1 h did not change the spatial EIS response of the segments other than to elicit the appearance of low-frequency inductance for segments 1-3 (Fig. 4 b). The operation without acetonitrile in the air stream for 3 h decreased the resistances of segments 1-4 and 10 and induced low-frequency inductive loops appearance for all segments, as was observed in the high current case (Fig. 2). The inductive loop was observed at the voltage range of 0.550-0.570 V, where the inflection point and extrema values of the current densities were detected. The presence of low-frequency inductance most likely indicated the occurrence of subsequent reactions involving the adsorbed CH₃CN species on the Pt catalyst. Segments 1, 2 and 10 restored or even improved their impedance performances; however, the other segments did not recover their impedance performances after 25 h of operation with air (Fig. 4 b).

A comparison of the spatial cell performance before (BOT) and after the CH₃CN test at 0.2 A cm⁻² (EOT (1)) is presented in Fig. 5, which shows the polarization curves for segments 1, 4, 7, and 10 and the entire cell for a H₂/air gas configuration. The IV curves represent the trend observed for the whole cell. It is clear that CH₃CN poisoning at low current densities resulted in a significant decrease in the MEA activity. Moreover, the HFR increased in segments 4-9 in the range of 0.006-

0.023 $\Omega \text{ cm}^2$, and an ECA loss of 21.94% and 19.3% was observed for the anode and the cathode, respectively (Fig. 6 (a, b))

After the VI measurements at H_2/air condition, the cell was kept overnight at a constant 0.6 V voltage. The voltage and current density profiles of the segments are shown in Fig. 7. The initial total current produced by the cell was 72 A (or 0.95 A cm^{-2}), and the performances of segments 3-9 were lower than expected. However, the operation of the cell for 6-9 h improved the performances of the segments and the overall cell, and the final current reached 99 A (1.3 A cm^{-2}). Thus, the operation of the cell at a high current recovered the performance due to a higher water production rate and the removal of CH_3CN and its conversion products at the electrodes. Additionally, the ECAs of the anode and the cathode were determined after the overnight operation, and the results confirmed the recovery of the Pt catalyst surface. When the ECAs between the overnight recovery (EOT (2)) and before the CH_3CN test (BOT) are compared, the ECA loss was 9.22% and 2.84% for the anode and the cathode, respectively (Figs. 6 a) and b).

The performance distributions shown in Fig. 6 c clearly demonstrates the improvement in the spatial activity after the overnight operation at high current density compared with the local performance immediately after the CH_3CN exposure at 0.2 A cm^{-2} (Fig. 5). A slight decrease in the performance of the inlet segments 1 and 2 of ~15 mV was observed at low current densities and 10-25 mV at high current densities. The outlet segments 8-10 also exhibited a decrease in the performance of 10-30 mV at 1.0-1.4 A cm^{-2} . Moreover, CH_3CN resulted in performance loss of all segments at 1.6 A cm^{-2} . The observed voltage losses were primarily due to a slight increase in the activation and mass-transfer overpotentials [54]. Acetonitrile exposures at low current densities resulted in a severe impact on PEMFCs and the ECA and HFR. The MEA could not restore its initial

performance after stopping the contaminant injection into the air stream. Such behavior was likely due to the effects of acetonitrile and its products on the catalyst surface and ionomers. The performance was only restored after a long-term operation (9-10 h) at a high current density because the produced water removed foreign compounds from the anode/cathode layers and membrane.

4. Discussion

In the past, oxygen electroreduction at Pt electrodes in the presence of CH₃CN was studied using the RDE and RRDE methods [43-47]. Acetonitrile was reported to poison the ORR, by strongly chemisorbing onto the Pt catalysts over a wide range of potentials, inhibiting hydrogen adsorption and platinum oxides formation. Moreover, CH₃CN caused a cathodic shift of the ORR potential with noticeable H₂O₂ formation. These observations indicated on changes in ORR mechanism from an efficient 4-electron to a 2-electron pathway [81, 82], which is not desired at fuel cell operations because H₂O₂ facilitates Nafion degradation and corrosion processes at gas diffusion electrode (GDE) [83-86].

Studies of CH₃CN electroadsorption on Pt by RDE demonstrated several possibilities of initial interactions between the electrode and the organic compound [30-33, 35, 41]. It was suggested that chemisorption occurred by donative mechanism through the lone electron pair on the nitrogen (species I) or associative way (species II), where both carbon and nitrogen atoms are conjugated with metal d-orbitals. This assumption was later confirmed by in-situ reflectance FTIR studies of chemisorbed CH₃CN on Pt [40].

Acetonitrile chemisorption was shown to be coupled with its reduction via two consecutive electron and proton transfer processes, where fast reversible process at 0.7-0.4 V followed by second slow reduction at 0.4-0.05 V due to steric limitations [30-32, 36]. During the second reduction the adsorbed CH_3CHN species needs to change its hybridization from a linear sp to a bent sp^2 imine type structure. These two consecutive reduction reactions correspond to a reversible broad reduction/oxidation peak (0.35-0.7 V) in the double layer region of the CV measurements [30-32, 35, 36, 41, 43-47].

Further studies have provided additional details regarding the possible reduction behaviors of acetonitrile on Pt [35, 41]. The chemisorption and surface reactivity behavior of CH_3CN was found to be specific to the geometry of Pt (110), (100), (111), (311). However, conclusions drawn from the structure of the chemisorbed intermediates are difficult to make based only on cyclic voltammetry and transient data alone. The application of in situ infrared spectroscopy has allowed the authors to add the following reactions and species into considerations.

Chemisorbed CH_3CN undergoes reversible stages of reduction/oxidation at 0.7-0.4 V and slower further reduction/oxidation at 0.4-0.05 V. This allowed us to assume that the observed inflection points in the voltage profiles at the initial stages of poisoning (0.48-0.50 V) and at recovery (0.52-0.55 V) were most likely attributed to this sequence of two electron acetonitrile reduction/oxidation reaction. Taking into account the HFR results (Figs. 1 and 4) and the assumption that the anode potential is ~ 0 V, the cathode potential (cell voltage compensated by the ohmic loss) is approximately equal to 0.49-0.58 and 0.53-0.63 V, respectively. Therefore, the transition between the two reversible reduction/oxidation stages occurs under the present fuel cell conditions at a higher electrode potential than the 0.4 V as reported in the literature. In addition, the slow second reduction/oxidation is likely responsible for the low-frequency inductance obtained during the recovery stage.

A gas chromatographic analysis of the cathode outlet gas of a PEMFC operated at steady state at 0.65 V showed the presence of CH_3CN , CH_3COOH , CH_3COH , CO_2 , NH_3 and traces of CO whereas the anode outlet gas did not contain any impurities [28, 87]. So acetonitrile only partially converted to the other products at the fuel cell cathode conditions (80°C , air, 48.3 kPa_g, 50% RH). A detailed analysis of the electrochemical reactions of CH_3CN on Pt at RDE conditions using on-line mass spectroscopy revealed that the electrooxidation of acetonitrile to CO_2 and to NO_x was observed at potentials greater than 0.7 V and 1.2 V, respectively [39]. The electroreduction of acetonitrile occurred at potentials below 0.1 V and resulted in the formation of C_2H_6 and NH_3 [34, 36, 39]. In

our experiments, the fuel cell was operated at 0.3-0.9 V, and we did not expect that such electrochemical reactions would take place.

Acetonitrile is expected to be hydrolyzed to acetic acid and ammonia via amide formation at the conditions of PEMFC according to the following equations:

Moreover, the imine type species IV can also be hydrolyzed in the presence of acids and elevated temperature with the formation of acetaldehyde and ammonia, which was assumed by B.E Conway [31, 32] and confirmed by of G. Horányi and E.M. Rizmayer [34].

The hydrolysis of CH₃CN and its derivative accounts for the presence of CH₃COOH, CH₃COH and NH₃ in the cathode outlet gas. Acetaldehyde can be easily oxidized by electrochemical way at the cathode, resulting in the formation of CO₂ and traces of CO [88-90], while acetic acid is most likely oxidized through a chemical mechanism [91-93].

Intensive studies of ammonium ion effects on ORR demonstrated a decrease in Pt ECA and an increase in H₂O₂ formation [18, 94-96]. Moreover, PEMFC performance was shown to decrease during NH₃ introduction into H₂ or air gas streams [20, 97-101]. The observation was attributed to the fact that NH₃ reduced the proton conductivity through the **membrane and catalyst layers** and increased the HFR of a fuel cell. **The ionic resistance of both membrane and catalyst layers'**

ionomer contribute to the HFR. The ionic conductivity of the catalyst layer is the first HFR component to be affected by neutralization of H^+ by NH_3 , leading to an ammonium-form ionomer with a larger HFR value. Moreover, the loss in protonic conductivity in the electrode layers is detrimental as a protonic flux is required to maintain a constant current and it cannot be sustained after the protons have been significantly replaced by NH_4^+ ions [99]. Based on the activation energies of ion transport data, it is inferred that ammonium moves through the vehicle mechanism (or translational diffusion) in Nafion membranes instead of through mixed transport via the Grotthuss (or hopping) mechanism and vehicle motion in the case of protons [19, 102]. Ammoniated forms of the ionomer contain less water and thereby, impedes the mobility of ions within the membrane [19, 23, 103, 104]. The ionic mobility of NH_4^+ is lower than that of H^+ (i.e., $7.61 \cdot 10^{-4}$ and $3.625 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ at 25°C , respectively) [19, 23, 103-105]. It was also found that the kinetics of ammonia adsorption onto sulfonic groups at low humidity was much faster than at high humidity and that the operation of PEMFCs at high relative humidity enhanced their ammonia tolerance [104]. In addition, the ionic conductivity of an ammonium-contaminated ionomer depends on the water content with a higher water content leading to a larger conductivity [19].

Studies of CH_3CN effects on Nafion XL membranes did not show any increases in the membrane HFR [87]. Instead, HFR increased only under fuel cell operating conditions. Thus, we concluded that acetonitrile did not affect the ionomer by itself; its derivative, which can be produced at the Pt electrode under fuel cell conditions, caused the HFR decline. Therefore, acetonitrile hydrolysis provides an additional contaminant for PEMFC, i.e., ammonia, which with CH_3CN negatively influences the ORR and Pt ECA and reduces ionic conductivity. Moreover, a decrease in anode ECA observed after CH_3CN exposure at 0.2 A cm^{-2} (Fig. 6a) implies that the anode was also

affected. The diffusion of acetonitrile from the cathode to the anode is not favored due to its relatively significant molecular weight and characteristic diameter. However, the NH_4^+ as acetonitrile derivative accumulates in electrodes layers, promoting diffusion to the anode, resulting in a decrease in both ionic conductivity and anode ECA during long-term operation (~105 h) [95, 99]. The anode NH_4^+ poisoning contribution to the PEMFC performance loss is relatively negligible in comparison to the cathode CH_3CN and NH_4^+ poisoning contribution and ohmic losses due to the HFR increase.

The impact of contamination on the spatial HFR and current densities was found to be severe in the case of low current density operations, when water production at the cathode is not high (Fig. 3). It is possible to assume that at high current densities, the produced water could remove NH_3 and CH_3CN from the cathode GDE and mitigate any negative effects because both contaminants are miscible with water. At low current density operations, acetonitrile and ammonia can be accumulated in the catalyst layer and the ionomer causing a considerable increase in the HFR and performance loss. Due to this reason, operations at high current densities were required to restore cell performances after CH_3CN exposure at 0.2 A cm^{-2} .

The observed spatial performance and previously published data are consistent with the following mechanism (Fig. 8). At the beginning of acetonitrile exposure, CH_3CN chemisorbs and hydrolyzes to acetic acid and ammonia, causing a performance loss due to their negative effects on the ORR, a decrease in the current density for the inlet segments and an increase for the outlet. The formation of NH_3 as a product of acetonitrile hydrolysis results in an increase in the local HFR, as was detected by EIS. At the same time, the chemisorbed acetonitrile reduces via two reversible, consecutive electron and proton transfer processes, wherein a first fast step is followed by a second

slow reduction. The detected inflection point at $\sim 0.48\text{-}0.50$ V appears to be the point where the second reduction begins. As soon as reduction occurs, the current density for the inlet segments increase, while those for the outlet ones decreases. The product of the acetonitrile reduction, i.e., an imine-like structure, is prone to hydrolysis with the formation of acetaldehyde and ammonia. Acetic acid and acetaldehyde can be partially oxidized to CO_2 by electrochemical or chemical mechanisms on Pt and in presence of oxygen. Because NH_3 and CH_3CN are soluble, the water produced at the cathode participates in their transport downstream, which can explain the order of the HFR and current density distributions at steady state, especially during low current density operations. During recovery, the same two consecutive electron and proton transfer reactions cause an inflection point in the voltage profiles at $\sim 0.52\text{-}0.55$ V and extremum values at the local current densities. Based on the spatial EIS data and the observation of the low-frequency inductance at a potential of 0.55 V, the second process appears to be slower than ORR. The inductance implies that the current signal follows a perturbation with a phase delay, which can be explained assuming a coverage relaxation slowness of the adsorbed acetonitrile intermediates: the coverage decreases with an increasing perturbation current signal, but it takes some time for establishing a new steady state [73, 76-79]. The cell recovery strongly depends on the operating current density and humidification of the cathode gas stream.

5. Conclusions

The spatial performance of a PEMFC exposed to 20 ppm CH_3CN was studied using a segmented cell under different operating current densities. Acetonitrile poisoning resulted in current density redistributions and voltage losses of 0.380 and 0.290 V at 0.2 and 1.0 A cm^{-2} , respectively. The current distribution ranged from +12% to -15% at steady state in the case of 1.0 A cm^{-2} , whereas at 0.2 A cm^{-2} , a steady state was not reached.

The observed current redistribution is explained by the chemisorption of CH_3CN and the subsequent two reversible consecutive electron and proton transfers, i.e., reduction/oxidation reactions, of the adsorbed CH_3CN species. The hydrolysis of CH_3CN and an intermediate imine structure resulted in NH_3 formation, an additional cathode contaminant. Together, ammonia and acetonitrile significantly affected the ORR, Pt ECA and HFR and decreased the cell performance. Other products of hydrolysis can be partially oxidized to CO_2 under fuel cell conditions. Spatial EIS data revealed an increase in the HFR and cathode charge transfer and mass transfer resistances during poisoning. A pseudo-inductive behavior at a low frequency was observed after 1-3 h of recovery most likely due to a slow transformation of the intermediates on the Pt surface.

After switching to pure air, the cell performance completely recovered within 4 h at 1.0 A cm^{-2} ; while recovery was not complete at 0.2 A cm^{-2} . However, the cell restored its performance after 10 h of operation at high current densities. Because NH_3 and CH_3CN are miscible with H_2O , the cell performance under contaminant exposure was strongly dependent on the operating conditions (current density) and water production, the higher the operating current density, the less severe the impact on the PEMFC. Fuel cell operations at high current densities or at 100% cathode RH may be considered as mitigation options.

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Fig. 1

Fig. 2

Fig. 2

Fig. 3

Fig. 4 a

Fig. 4 a

a)

Fig. 4 b

Fig. 4 b

b)

Fig. 5

Fig. 6 a

Fig. 6 b

Fig. 6 c

Fig. 7

Fig. 8

Figures captions

Fig. 1. Voltage (a), normalized current densities and high-frequency resistance (b) of individual segments vs. time for an overall current density of 1.0 A cm^{-2} and 20 ppm CH_3CN . Anode/cathode: H_2/air , $1.059/2.522 \text{ l min}^{-1}$, 100/50% RH, 48.3/48.3 kPa_g, 80°C.

Fig. 2. EIS for segments 1-10 and the overall cell during 20 ppm CH_3CN exposure test at 1.0 A cm^{-2} . Anode/cathode: H_2/air , $1.059/2.522 \text{ l min}^{-1}$, 100/50% RH, 48.3/48.3 kPa_g, 80°C.

Fig. 3. Voltage and high-frequency resistance (a), normalized current densities (b) of individual segments vs. time for an overall current density of 0.2 A cm^{-2} and 20 ppm CH_3CN . Anode/cathode: H_2/air , $0.422/1.009 \text{ l min}^{-1}$, 100/50% RH, 48.3/48.3 kPa_g, 80°C.

Fig. 4. Spatial EIS for segments 1-10 and the overall cell during 20 ppm CH_3CN exposure at 0.2 A cm^{-2} (a) and at recovery (b). Anode/cathode: H_2/air , $0.424/1.009 \text{ l min}^{-1}$, 100/50% RH, 48.3/48.3 kPa_g, 80°C. The results present spatial behavior within first 94 h of the test.

Fig. 5. VI curves for segments 1, 4, 7, 10 and for the whole cell before (BOT) and after (EOT (1)) 20 ppm CH_3CN exposure test at 0.2 A cm^{-2} . Anode/cathode: H_2/air , 2/2 stoichiometry, 100/50% RH, 48.3/48.3 kPa_g, 80°C.

Fig. 6. Distribution of differences in the anode (a) and cathode (b) ECAs between after the CH_3CN exposure (EOT (1))/overnight recovery (EOT (2)) and before the contamination test (BOT). Anode/cathode: H_2/N_2 (for ECA cathode), N_2/H_2 (for ECA anode), $0.750/0.750 \text{ l min}^{-1}$, 100/100% RH, ambient pressure, 35°C, scan rate 20 mV s^{-1} . Voltage distribution before (BOT) and after overnight recovery (EOT (2)) (c). Anode/cathode: H_2/air , 2/2 stoichiometry, 100/50% RH, 48.3/48.3 kPa_g, 80°C.

Fig. 7. Voltage (a) and current densities (b) of individual segments vs. time for a constant voltage operation at 0.6 V. Anode/cathode: H_2/air , $1.271/3.027 \text{ l min}^{-1}$, 100/50% RH, 48.3/48.3 kPa_g, 80°C.

Fig. 8. Schematic presentation of CH_3CN possible processes.